



## Letter to the Editor

## Comments on “Catalytic applications of red mud, an aluminium industry waste: A review”

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Recently, Sushil and Batra have been published the above-mentioned article in the journal Applied Catalysis B: Environmental [1]. In their review, they have done a comprehensive revision on the application of red mud to different catalytic processes, as coal-derivatives processing, catalytic hydrodechlorination or catalytic combustion.

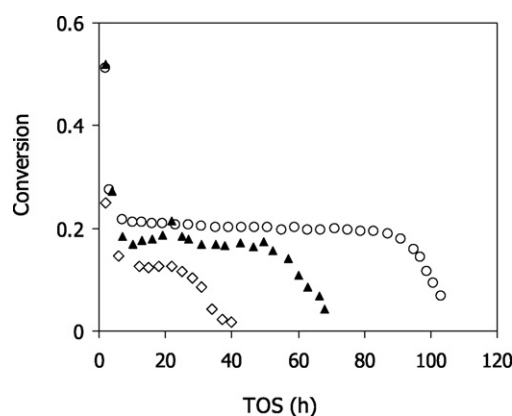
However I think that it is necessary to clarify several aspects concerning to how to improve the catalytic activity of this material. As the authors comment, red mud are used in oxidic form when reticular oxygen of the metal oxides (specially  $\text{Fe}_2\text{O}_3$ , hematite) plays a key role in the catalytic reaction (for example in combustion reactions), or in sulphided form, when the scope of the catalyst is to activate the hydrogen molecule (sulphides are more active than oxides for hydrogen activation). But, before considering this point, it must be taken into account that other constituents of the red mud, such as calcium and sodium oxides can interact with the major components, leading to crystallographic and morphologic changes at the reaction conditions required for most of the catalytic applications [2–4]. As in the case of other catalysts, these changes lead to a decrease of surface area and (also considering that red mud-based catalysts are bulk catalysts) to an activity decrease.

Because of these reasons, different authors have tried to develop procedures to remove these compounds, or to add new compounds that can compensate this negative effect. The first attempts were done by Pratt and Christoverson [5] in the early 1980s. These authors proposed a dissolution–precipitation method (basically, dissolution of the red mud in hydrochloric acid and precipitation with ammonia at pH 8), which decreases the Ca and Na red mud content, and increases its specific surface (ARM). This activation was observed to lead to higher activity and extended life periods for both hydrogenations (with sulphided catalysts) [6] and oxidations (in the oxidic form) [7].

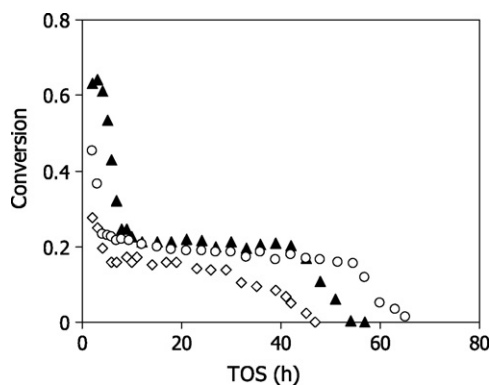
Inspired on this method, we have developed a new activation method. The modified activation method consists of the addition of

*ortho*-phosphoric acid to the hydrochloric acid for the leaching of the red mud. It was found that the addition of small amounts of P (up to around 4 wt% of P in the calcined catalyst, PARM) had a beneficial effect in the surface parameters and catalytic performance of this material, when compared to ARM, whereas higher amounts of P lead to sharp decreases in the surface area and hence poorer catalytic performance [2].

We have tested these catalysts, comparing the parent red mud and the red mud prepared according to the Pratt and Christoverson, with the red mud activated according to our procedure. This comparison has been done for two different reactions: selective hydrogenation of anthracene oil (in order to prepare partially hydrogenated anthracene oil, with important technological applications in pitch-like materials processing) and gas-phase



**Fig. 1.** Average conversion of the hydrogenable anthracene oil constituents (anthracene, pyrene, fluoranthene and fenanthrene) at 623 K and 10 MPa with untreated red mud (◇), red mud activated according to the method proposed in Ref. [5] (▲) and red mud activated by the method proposed in Ref. [2] (○). All the catalysts have been sulphided at the same conditions. Adapted from Ref. [2].



**Fig. 2.** Tetrachloroethylene conversions obtained at 623 K and 10 MPa with untreated red mud (◇), red mud activated according to the method proposed in Ref. [5] (▲), and red mud activated by the method proposed in Ref. [2] (○). All the catalysts have been sulphided at the same conditions. Adapted from Ref. [6].

tetrachloroethylene hydrodechlorination (in order to solve the environmental problem caused by the chlorinated wastes).

In the case of anthracene oil hydrogenation sulphided PARM perform better than ARM, both in terms of steady state activity and deactivation resistance, as observed in Fig. 1, showing a behavior very close to the corresponding to a commercial NiMo catalyst [8]. In addition, this catalyst presents higher selectivities to the most useful hydrogenated compounds.

Regarding to the hydrodechlorination reactions (Fig. 2), sulphided PARM presents slightly lower steady-state conversion than sulphided ARM, although PARM catalysts present higher resistance to HCl poisoning [6]. It was even observed, that PARM catalyst presents even higher HCl-poisoning resistance than commercial

hydrotreatment catalysts (supported NiMo sulphided catalysts) [9].

However, in the case of catalysts used in their oxidic form, as in the case of being used for methane catalytic combustion, our activation method does not provide any significant improvement of neither the catalytic activity nor the thermal stability of the catalysts [7].

In the review of Sushil and Batra, both kinds of activations are mixed and a little bit confused. So, I consider that it is necessary to point out the advantages of our activation method, especially for hydrogenation reactions.

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